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Three-Dimensional Composite Nanostructures for Lean NO_x Emission Control

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Project ID #
ACE030

Project Overview

Project Objective

–To develop a unique class of 3D metal oxide (MeO_x)/perovskite (ABO_3) composite nanostructure catalysts to reduce and control lean NO_x emission in vehicles, eventually to replace or reduce the usage of the Pt-group metal catalysts.

Timeline

- Project start date: 10/01/2009
- Project end date: 03/31/2013
- Percent complete: continuing

Budget

- Total project funding
  - DOE share: $1,248,242
  - Contractor share: $314,504
- Funding received in FY10-12 from DOE: $1,020,262

Barriers

- Barriers addressed
  - Lean NOx emission reduction
  - Particulate filtering using new catalysts
  - New catalysts for reducing/eliminating usage of noble metals
  - Simplification of emission control devices to reduce the cost

Partners

- HRI, UTRC, Umicore Autocat. USA Corning, Inc.; BNL

Objectives and Approaches

- Objectives (quarters 7-10, 04/1/2011-3/31/2012)
  - Optimization of synthesis of 3D nanoarray catalysts.
  - Metal loading and thermal/mechanical stability testing
  - Modeling of surface NO_x catalytic chemistry on perovskite surfaces.

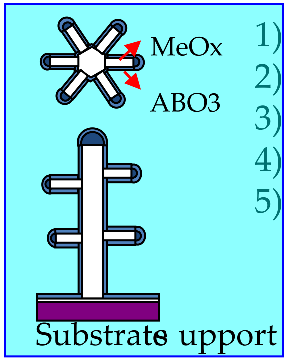
- Approaches:

➢ **Synthesis:**

To synthesize 3D composite nano(wire/dendrite)arrays rooted on different substrates by solution and vapor phase approaches.

➢ **Characterization:**

To investigate the structure, morphology, chemical and electronic properties of composite nanorrays using a range of microscopy and spectroscopy techniques.



1) Ultrahigh surface;
2) High thermal stability;
3) Strong adherence;
4) Low cost;
5) High tailoring ability

➢ **Activity, Stability, Durability and Regenerability:**

To explore the catalytic behavior and stability using microscopy, spectroscopy, thermal analysis and temperature programmed surface analysis tools.

➢ **Surface Catalysis Modeling :**

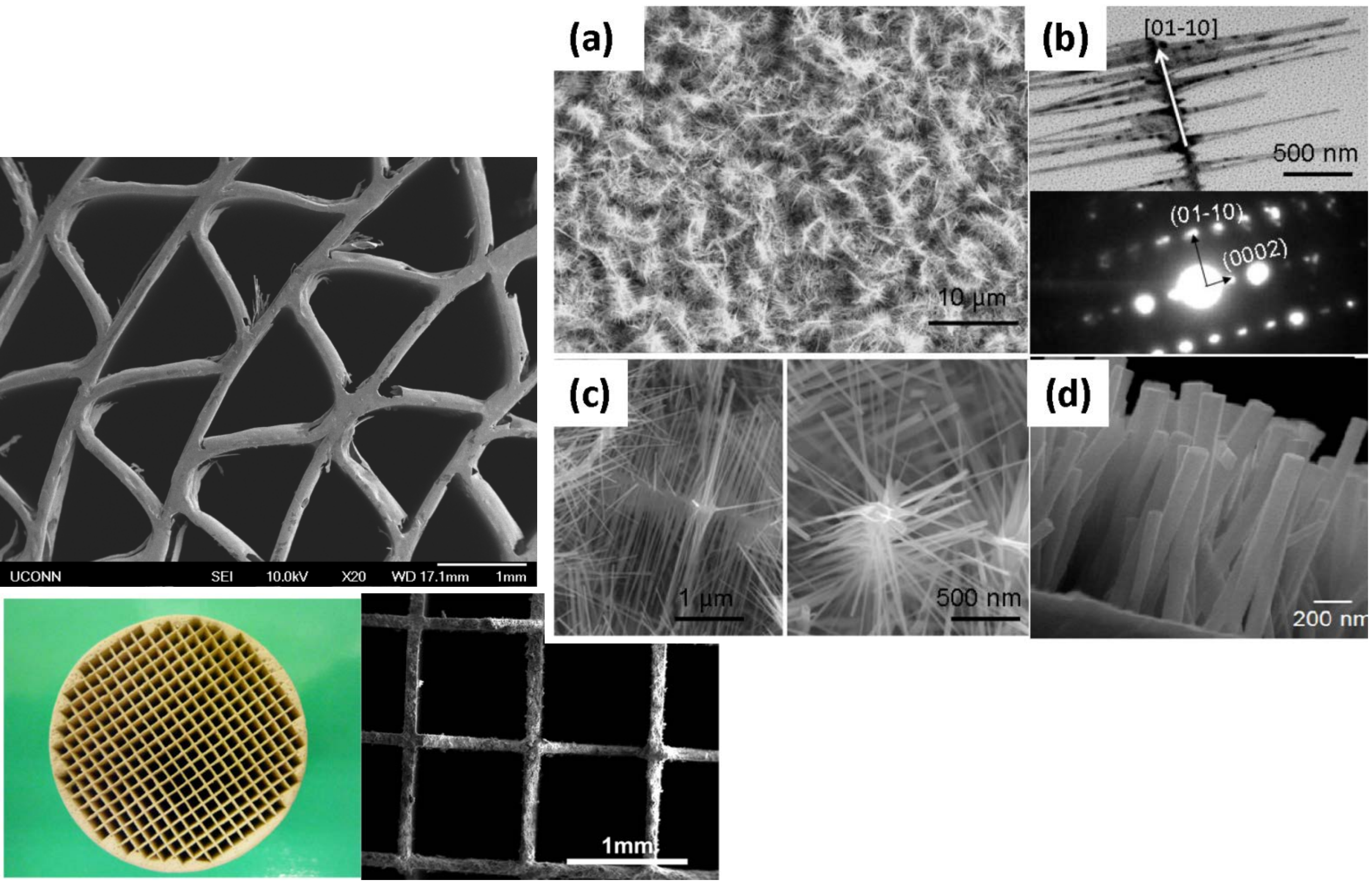
To simulate and model the surface catalysis behavior on composite nanocatalyst surfaces and interfaces using DFT atomistic calculation.

Accomplishments

(Project period: 04/1/2011-03/1/2012)

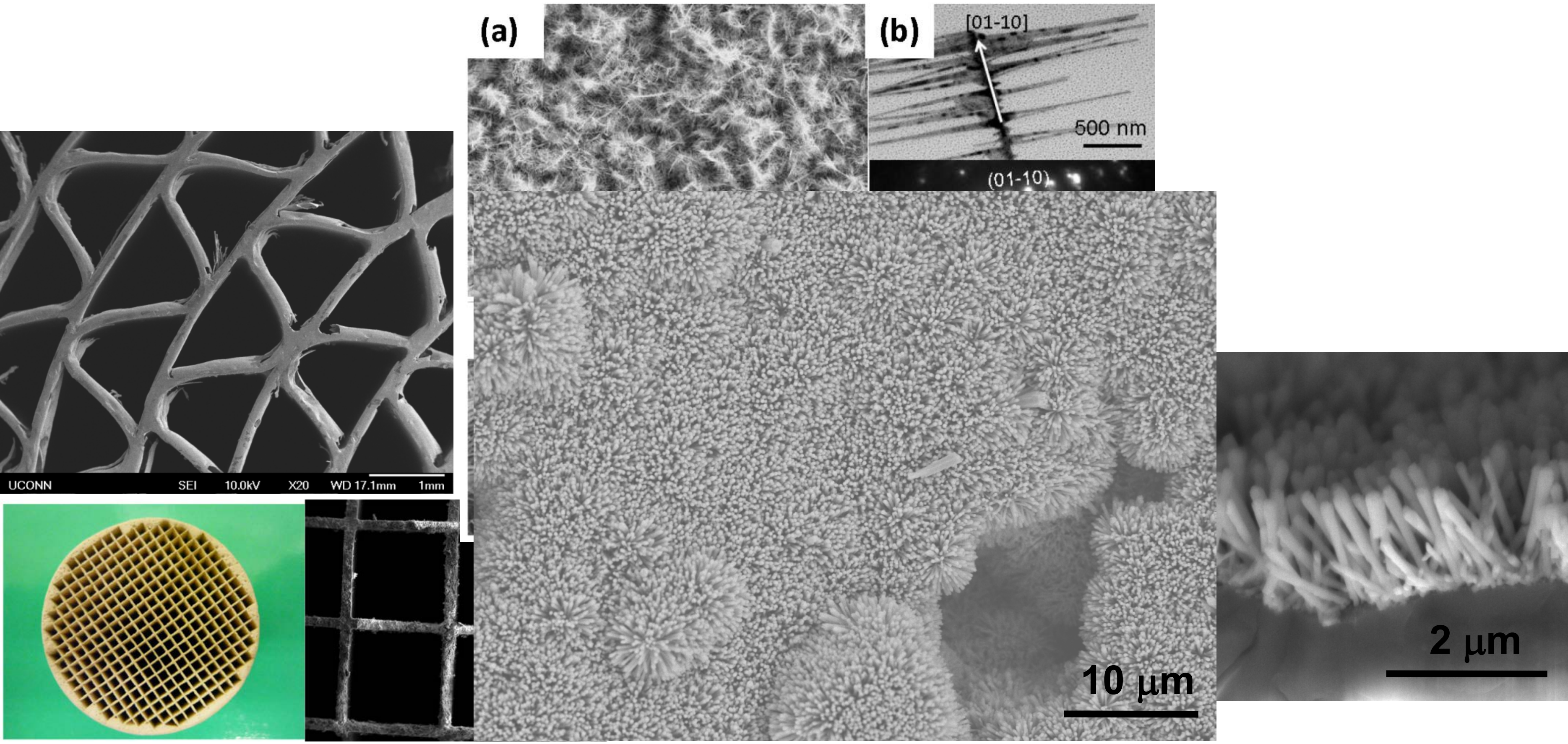
1) Synthesis, characterization and identification of various 3D composite nanowire monolithic catalysts with very high specific surface area.
2) Validation of the thermal stability of various composite nanowires on monolith substrates under both oxidative and reductive atmospheres, as well as the hydrothermal stability.
3) Emission testing over CO oxidation, NO oxidation, storage and reduction, and S-poisoning resistance.
4) Kinetic Monte Carlo simulation of the NO and O_2 surface catalytic interaction with perovskite crystal surfaces.

Large scale metal oxide nano-arrays grown in monolithic substrates



Metal oxide nano-array monolithic catalysts: Robust, Well-defined, Tunable.

Large scale metal oxide nano-arrays grown in monolithic substrates



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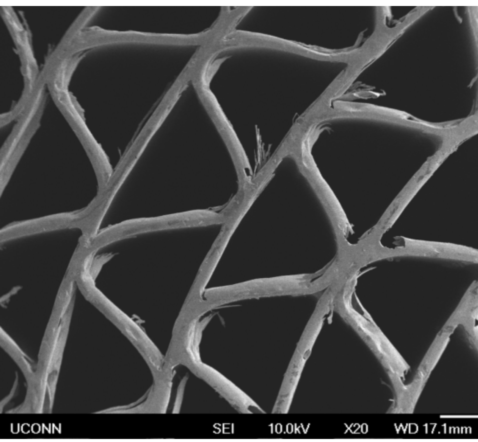
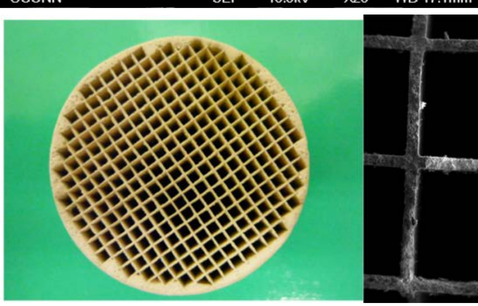
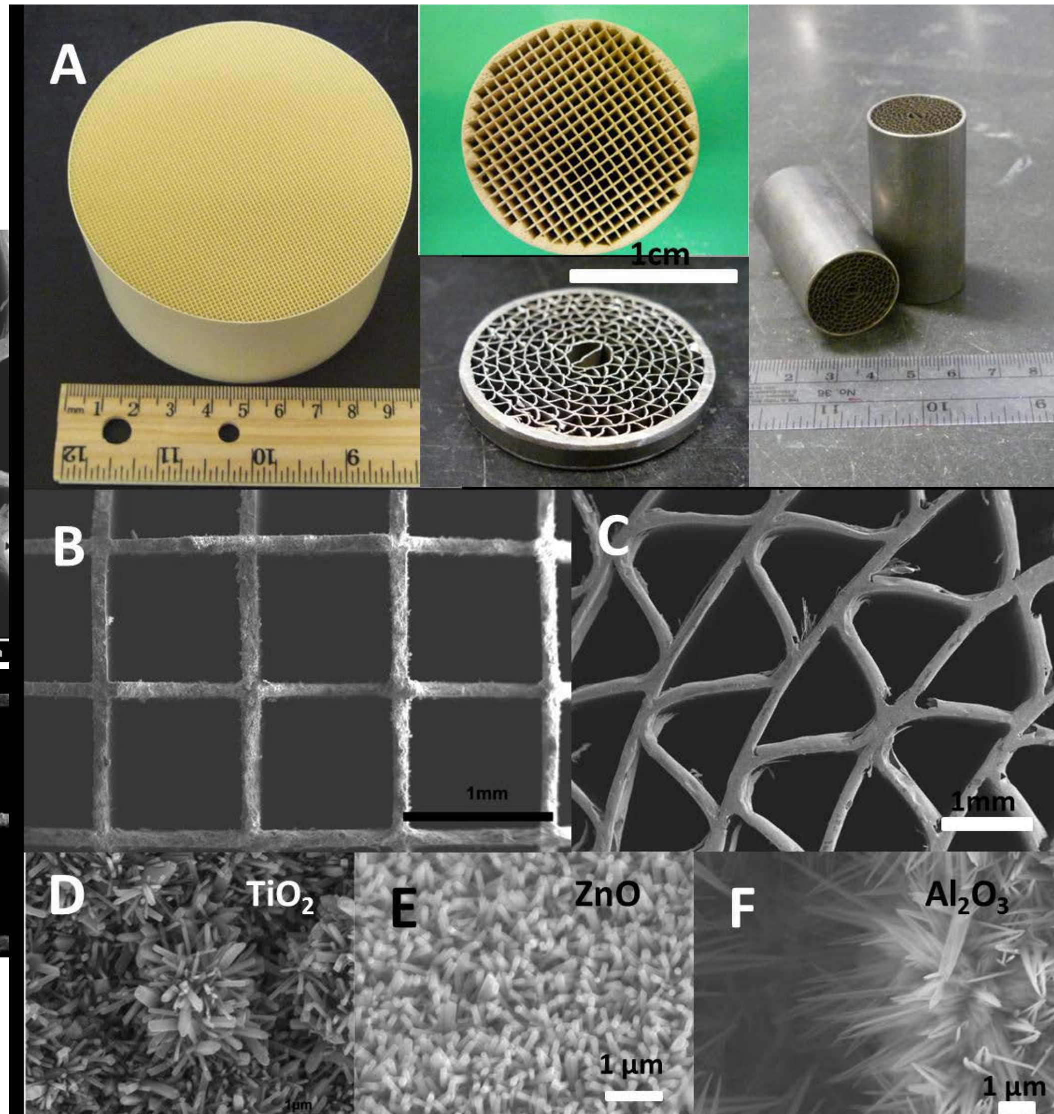
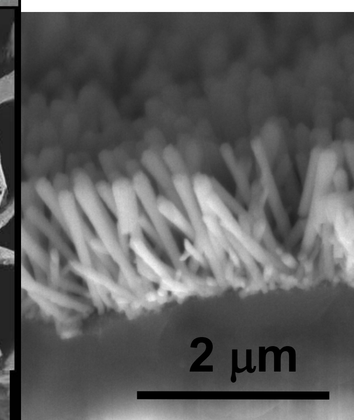




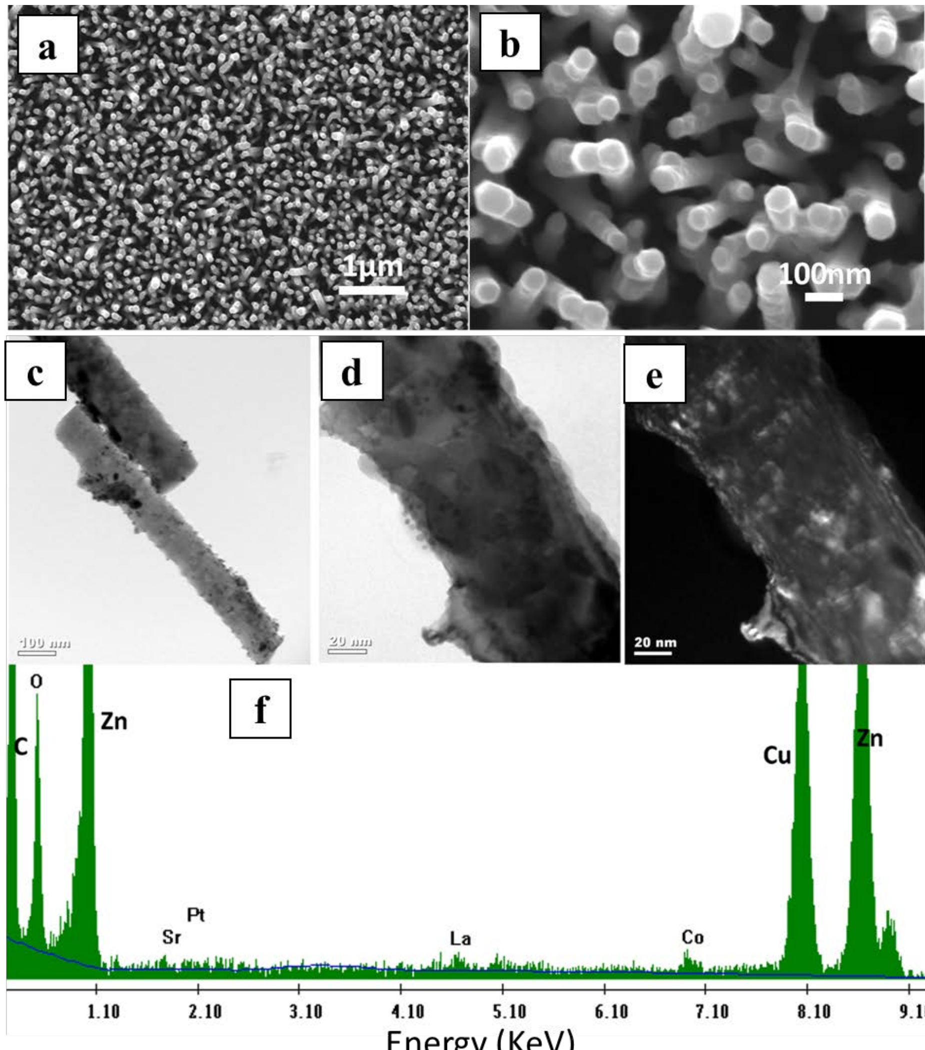




Metal oxide nano-array monolithic catalysts: Robust, Well-defined, Tunable.

Composite nanowire array catalysts

* In co-deposition and sequential deposition of Pt and LSCO on ZnO NWs, Pt ~ 1-4 wt.% over ZnO, < 0.01-0.1 wt.% over total monolithic catalyst.



Sequential deposition

1)ZnO

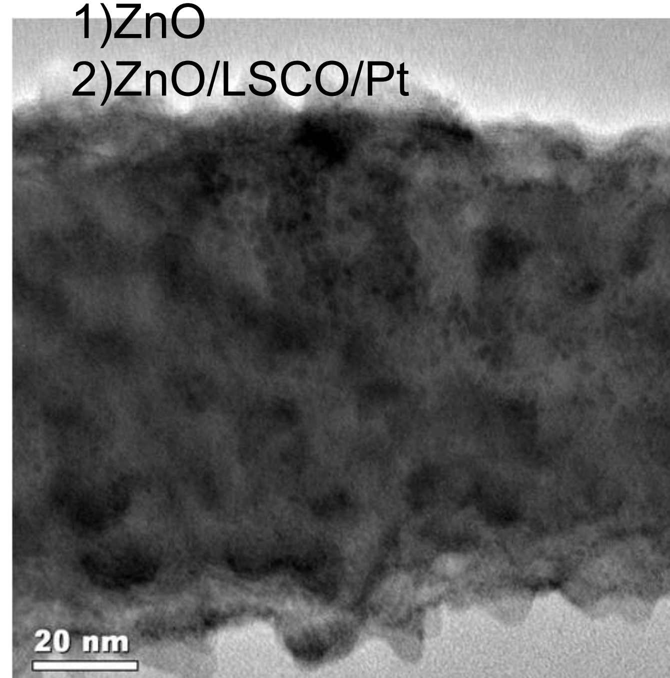
2)ZnO/LSCO

3)ZnO/LSCO/Pt

Or **co-deposition of LSCO/Pt**

1)ZnO

2)ZnO/LSCO/Pt

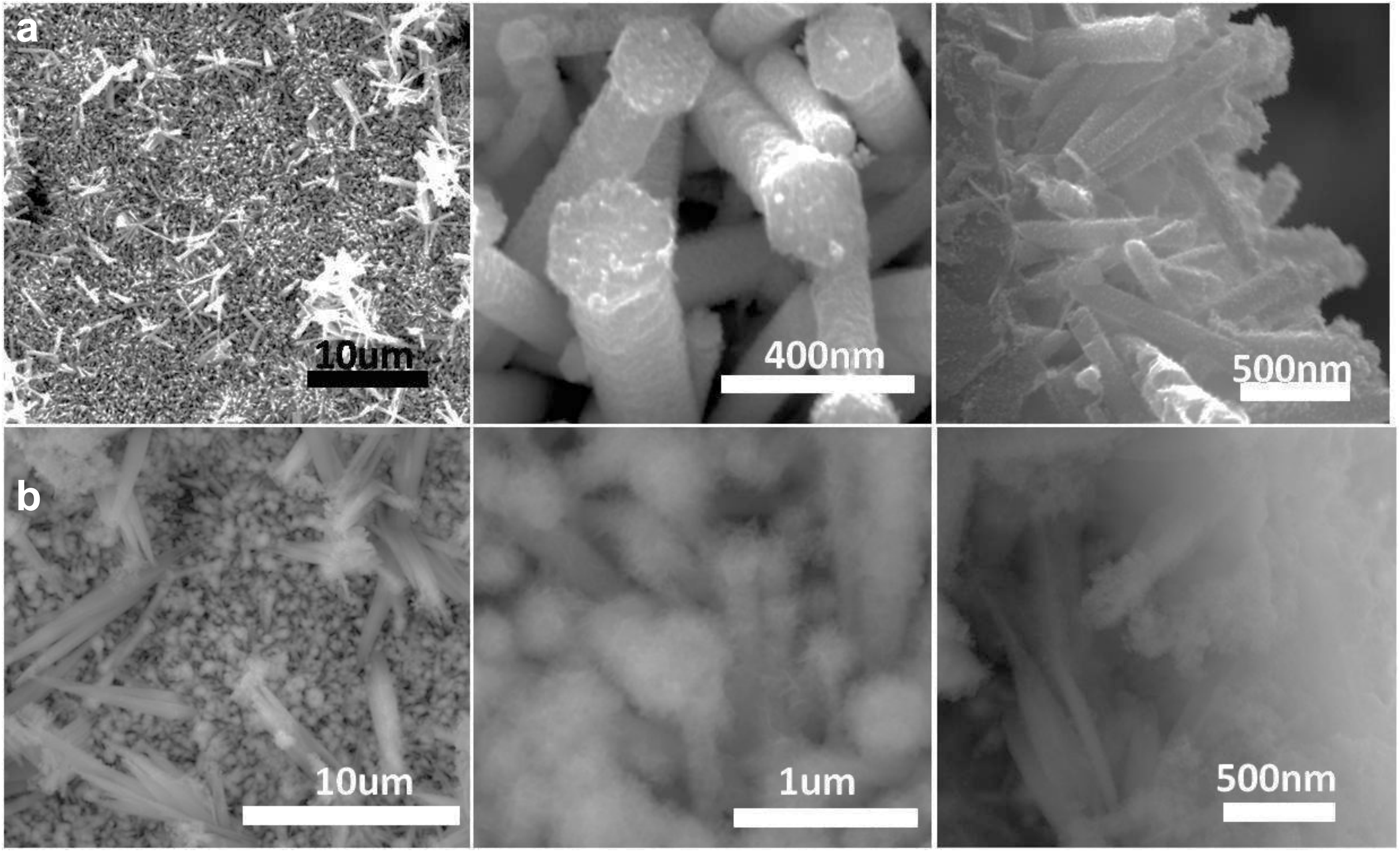


Composite nanowire array catalysts → Hydrothermal stability

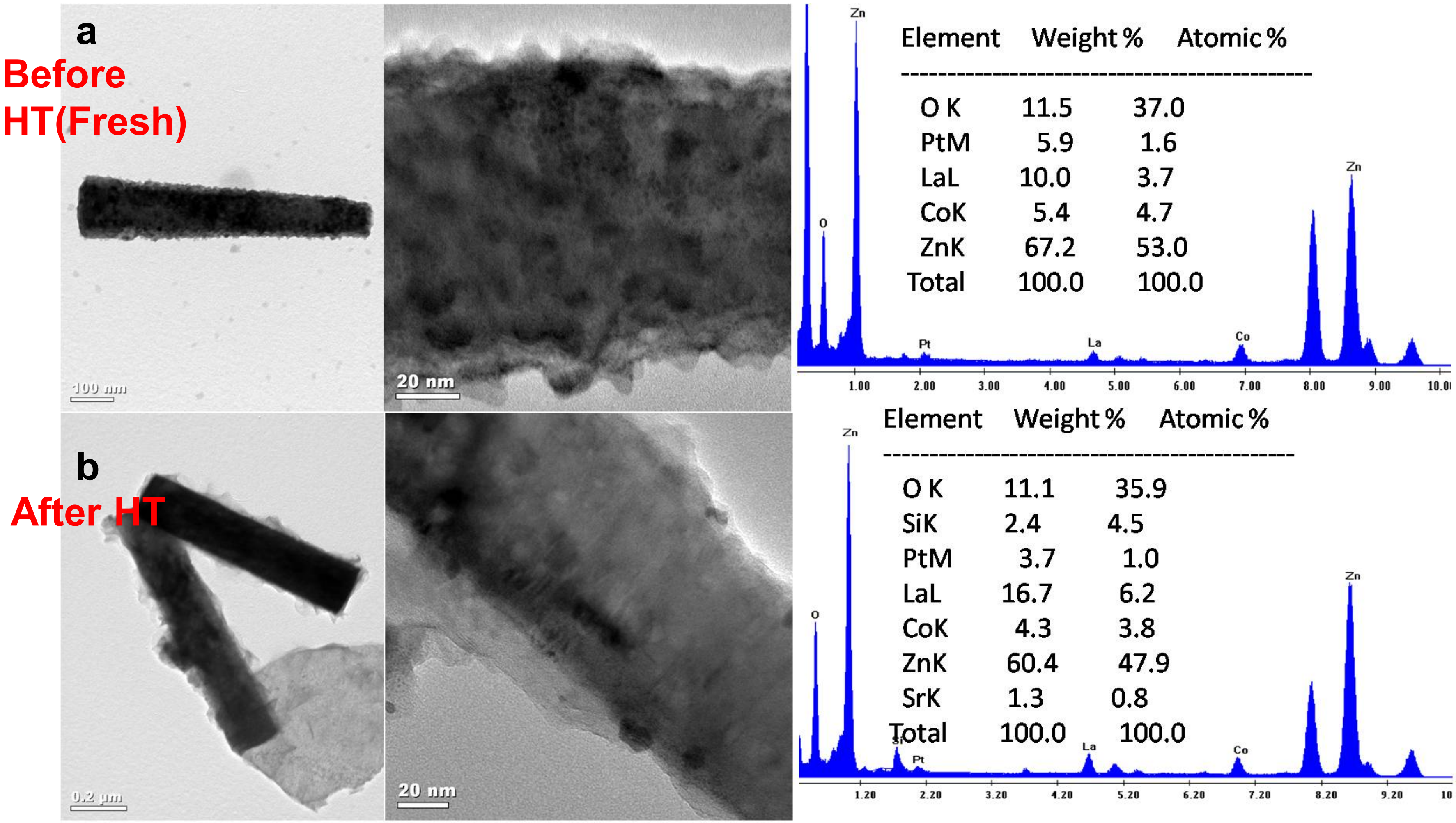
Hydrothermal Treatment (HT): 10% water vapor, 500 ^{o}C, 24h

Before HT(Fresh)

After HT



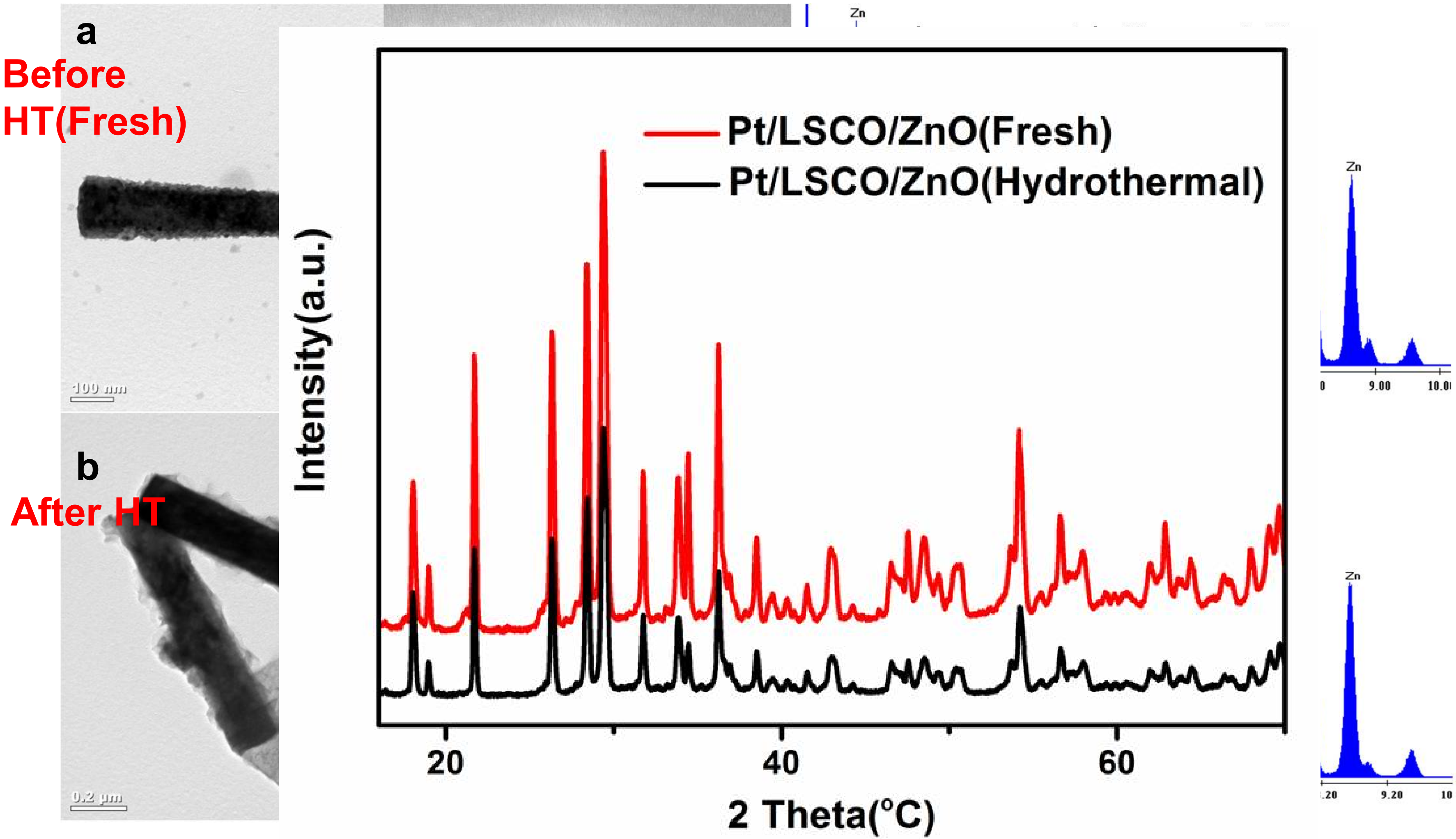
Composite nanowire array catalysts → Hydrothermal stability



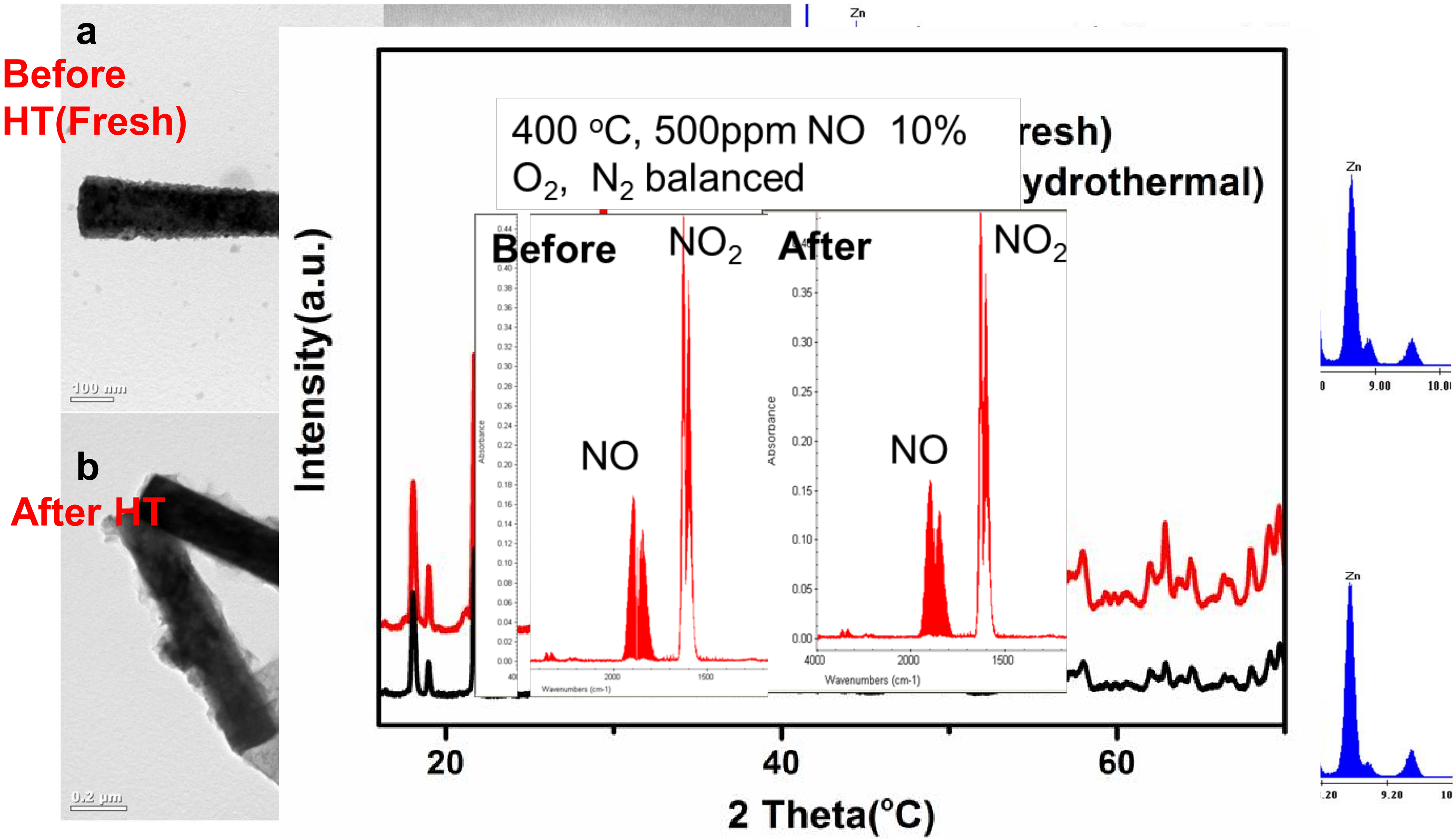
Element	Weight %	Atomic %
O K	11.5	37.0
PtM	5.9	1.6
LaL	10.0	3.7
CoK	5.4	4.7
ZnK	67.2	53.0
Total	100.0	100.0

Element	Weight %	Atomic %
O K	11.1	35.9
SiK	2.4	4.5
PtM	3.7	1.0
LaL	16.7	6.2
CoK	4.3	3.8
ZnK	60.4	47.9
SrK	1.3	0.8
Total	100.0	100.0

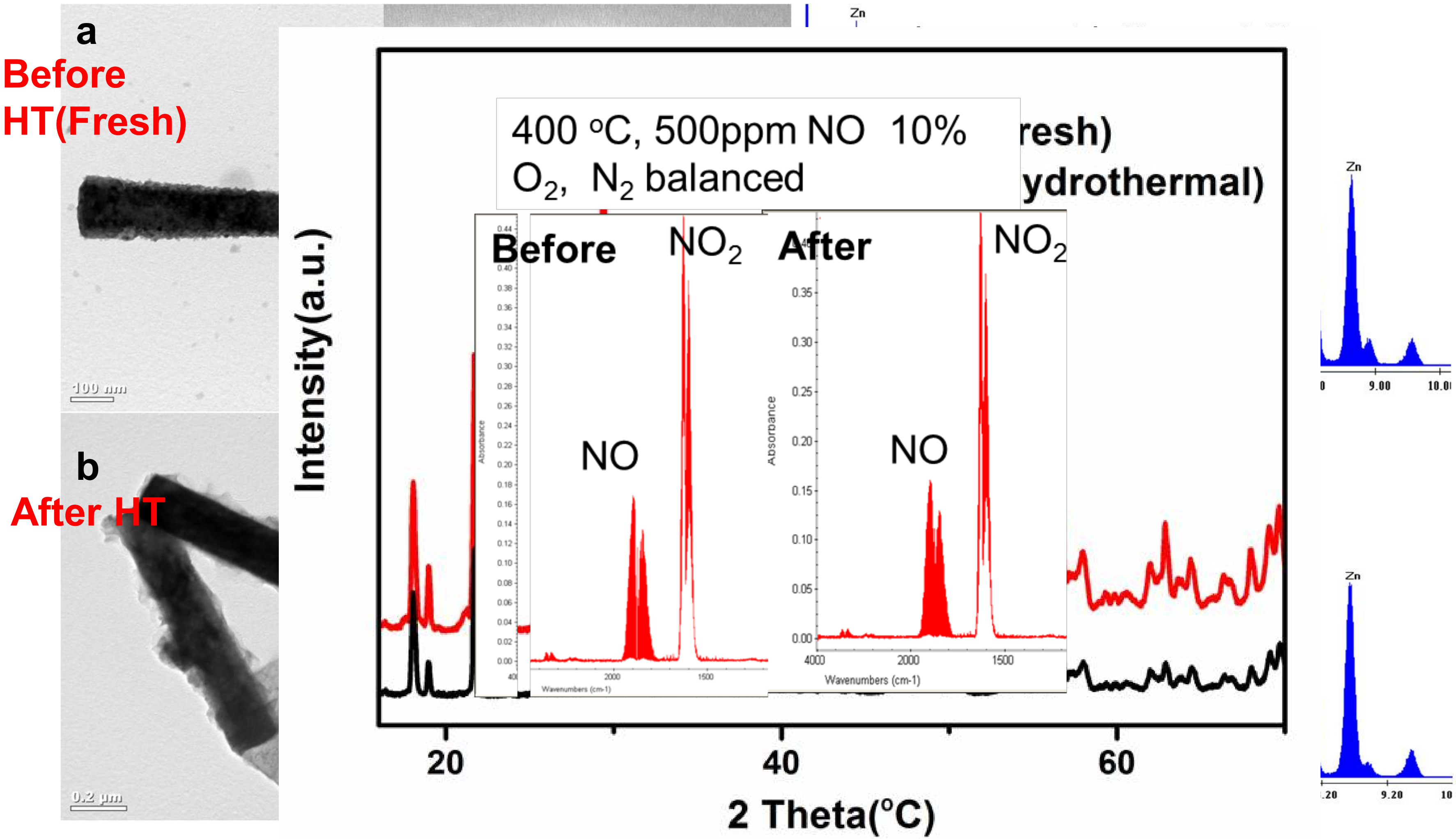
Composite nanowire array catalysts → Hydrothermal stability



Composite nanowire array catalysts → Hydrothermal stability



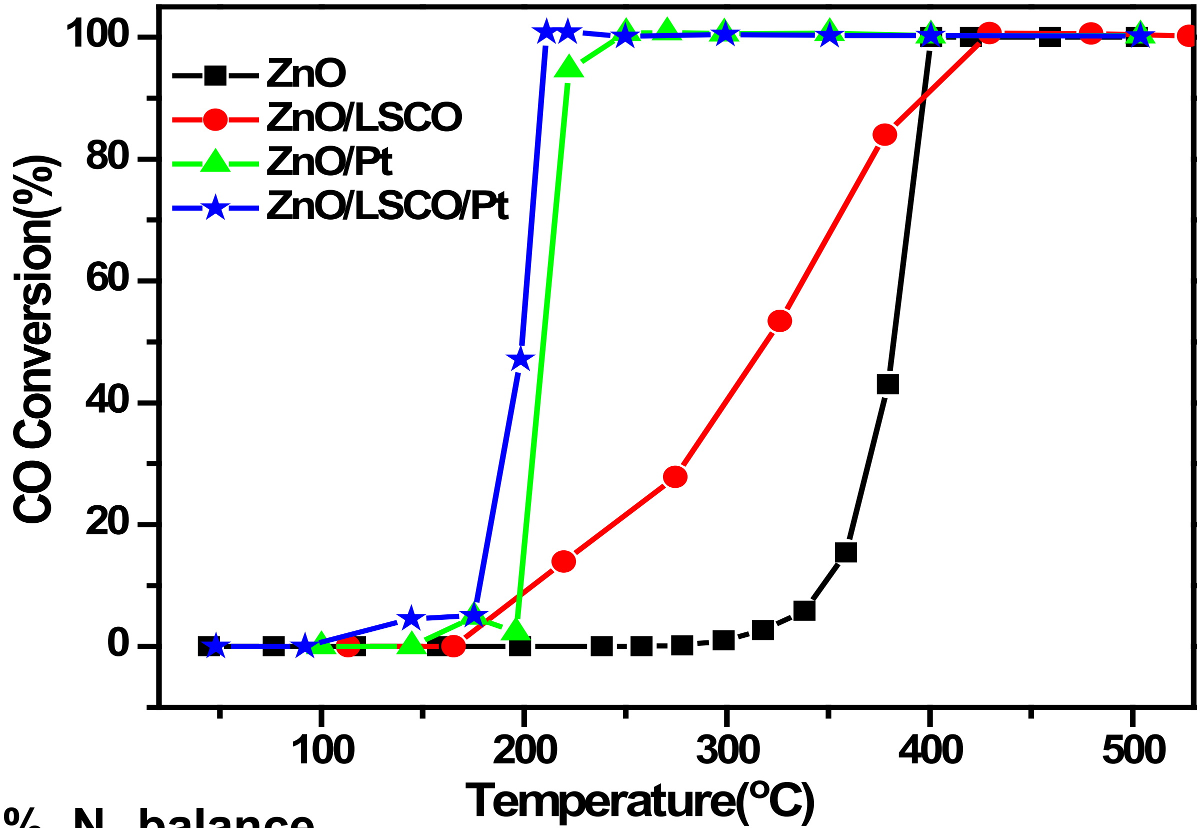
Composite nanowire array catalysts → Hydrothermal stability



- ✓ Structure and morphology to a good extent retained for nanocatalysts;
- ✓ NO oxidation activity maintained in selective nanocatalysts.

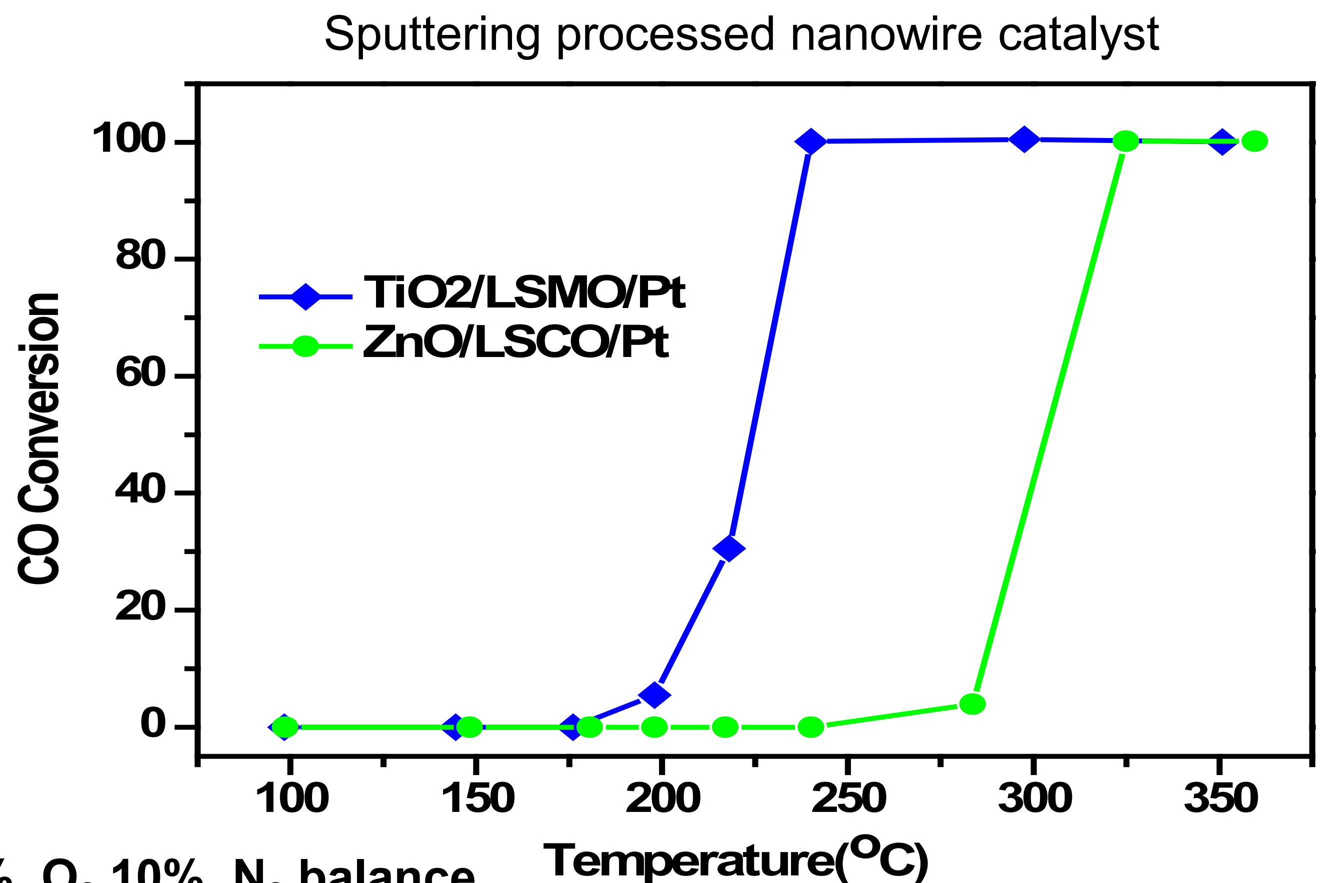
CO oxidation behaviors of composite nanowire array catalysts

Sol-gel processed nanowire catalylsts



CO 1%, O_2 10%, N_2 balance
Pt: <1 wt.% over ZnO; SV:45,454 h^{-1}

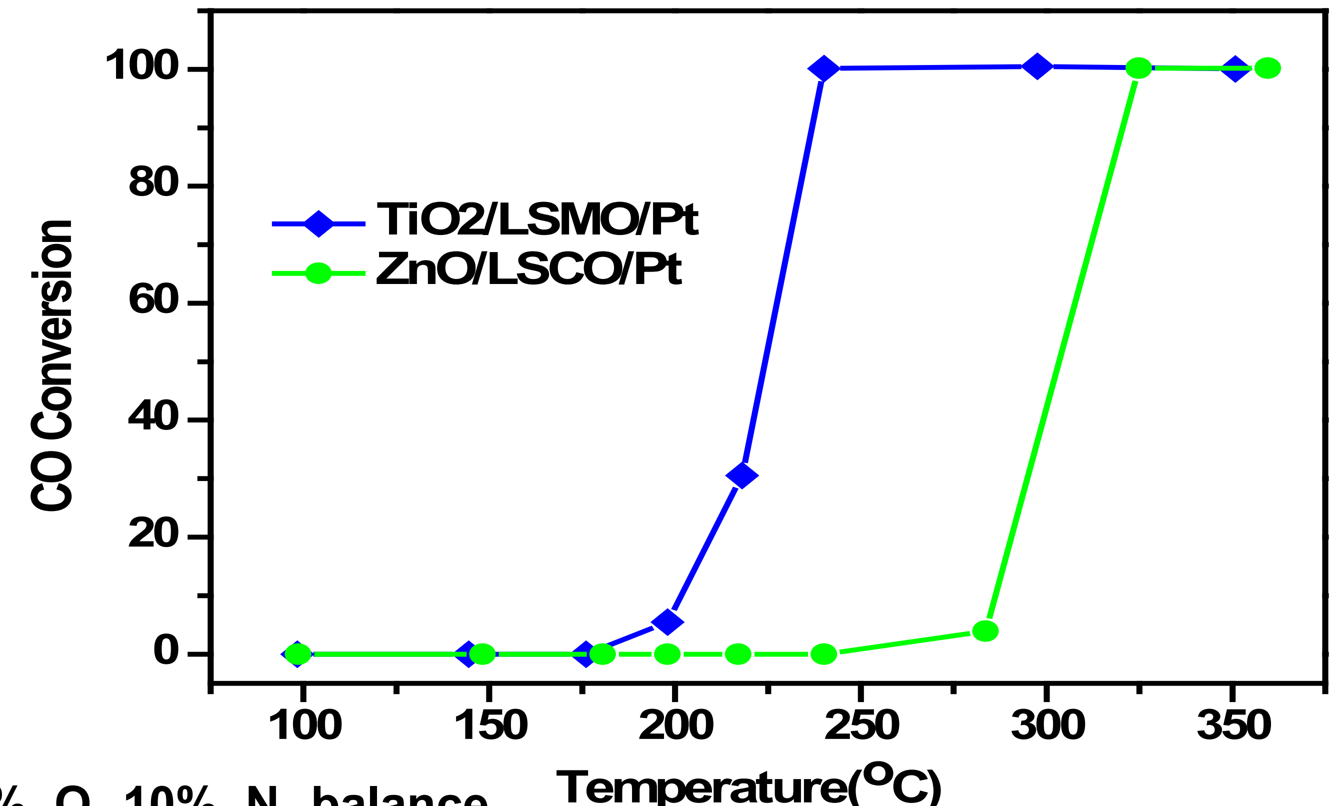
CO oxidation behaviors of composite nanowire array catalysts



CO 1%, O_2 10%, N_2 balance
Pt: <1 wt.% over ZnO; SV:45,454 h^{-1}

CO oxidation behaviors of composite nanowire array catalysts

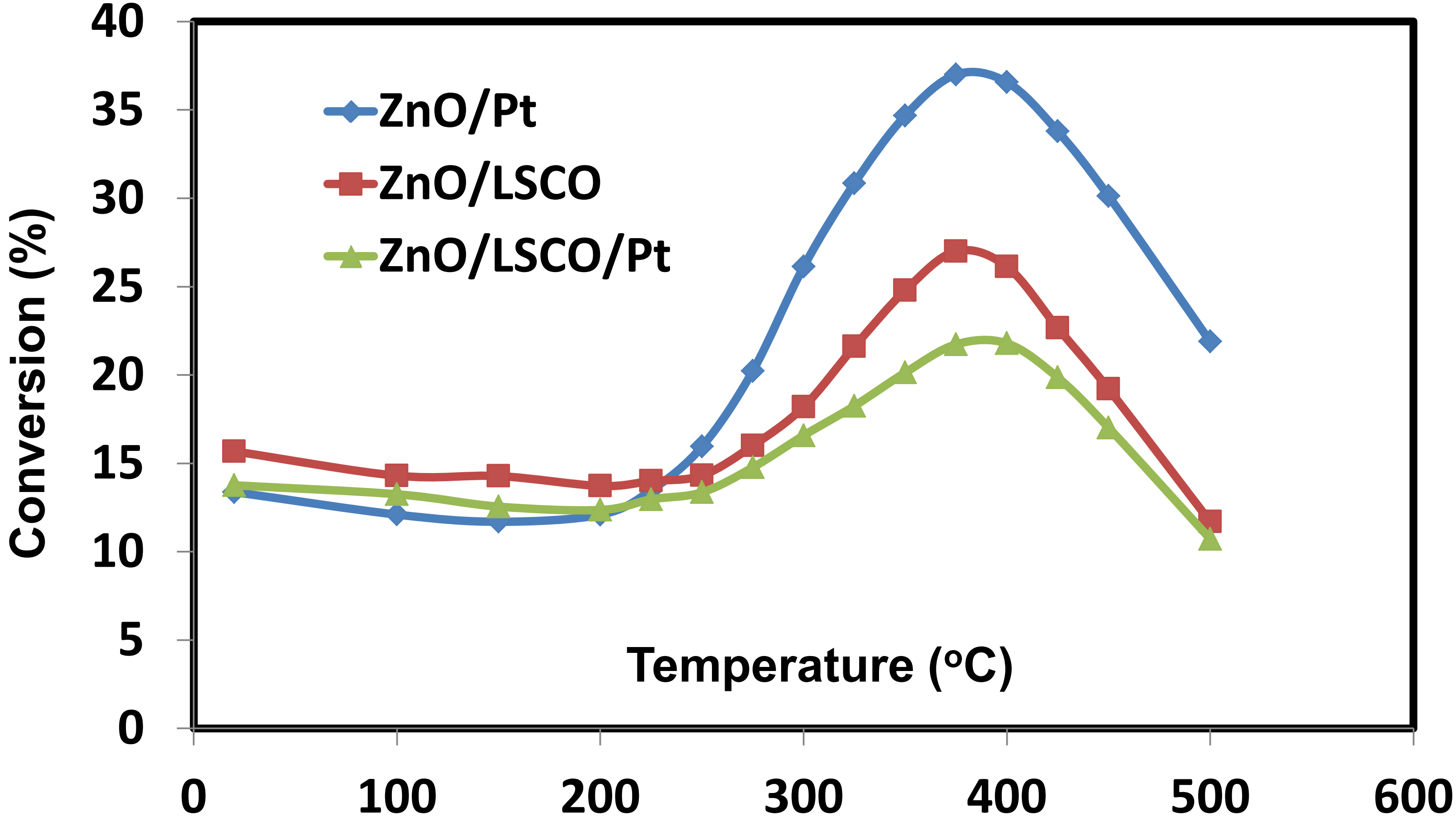
Sputtering processed nanowire catalyst



CO 1%, O_2 10%, N_2 balance
Pt: <1 wt.% over ZnO; SV:45,454 h^{-1}

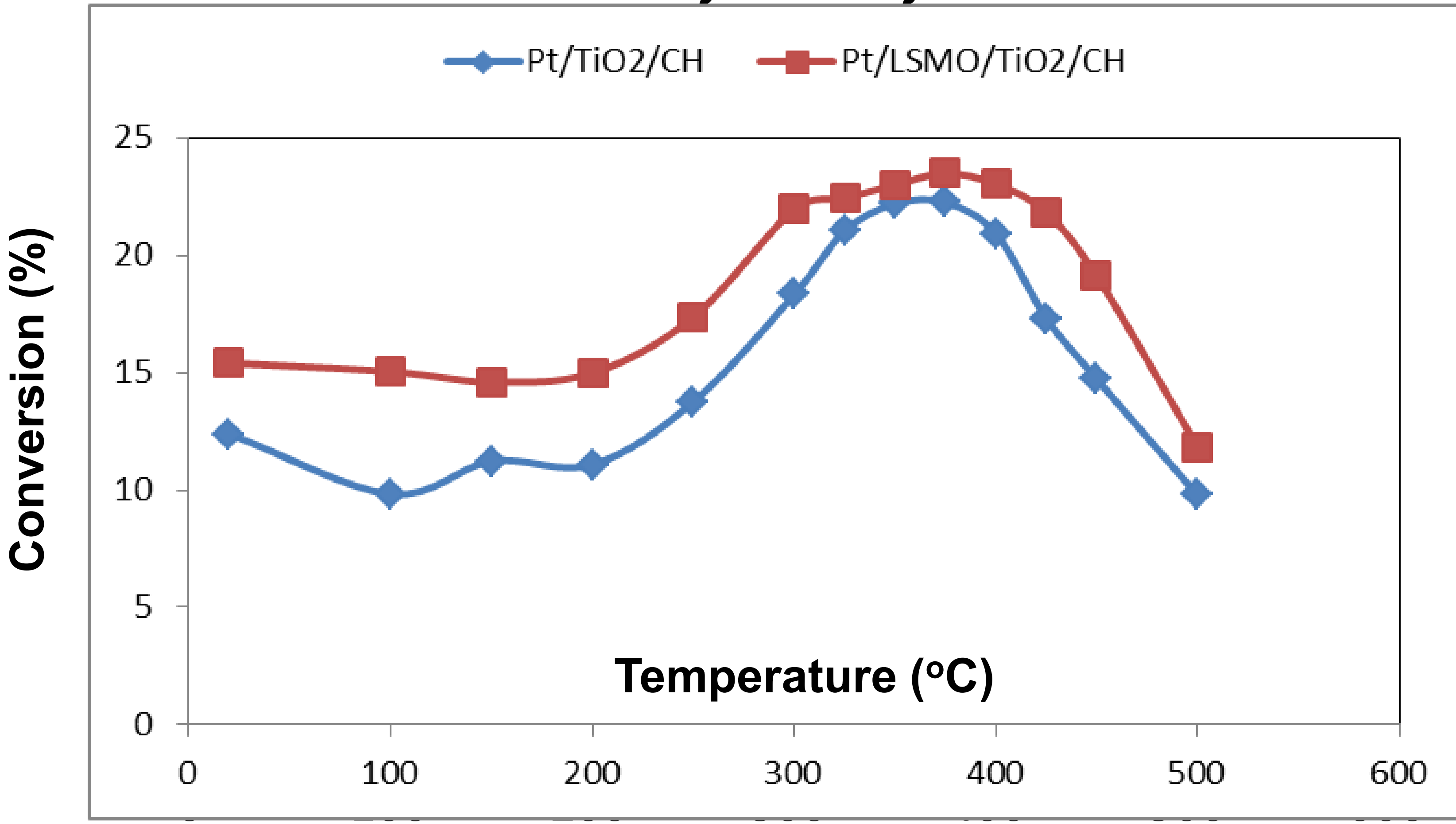
- ✓ Better performance in sol-gel processed nanowire catalysts;
- ✓ LSCO reduces the light-off temp in CO oxidation;
- ✓ TiO2/LSMO/Pt is better than ZnO/LSCO/Pt for CO oxidation.

NO oxidation behaviors of composite nanowire array catalysts



NO 500ppm, O_2 10%, N_2 balance; Pt: <1%; SV:166,667 h^{-1}

NO oxidation behaviors of composite nanowire array catalysts



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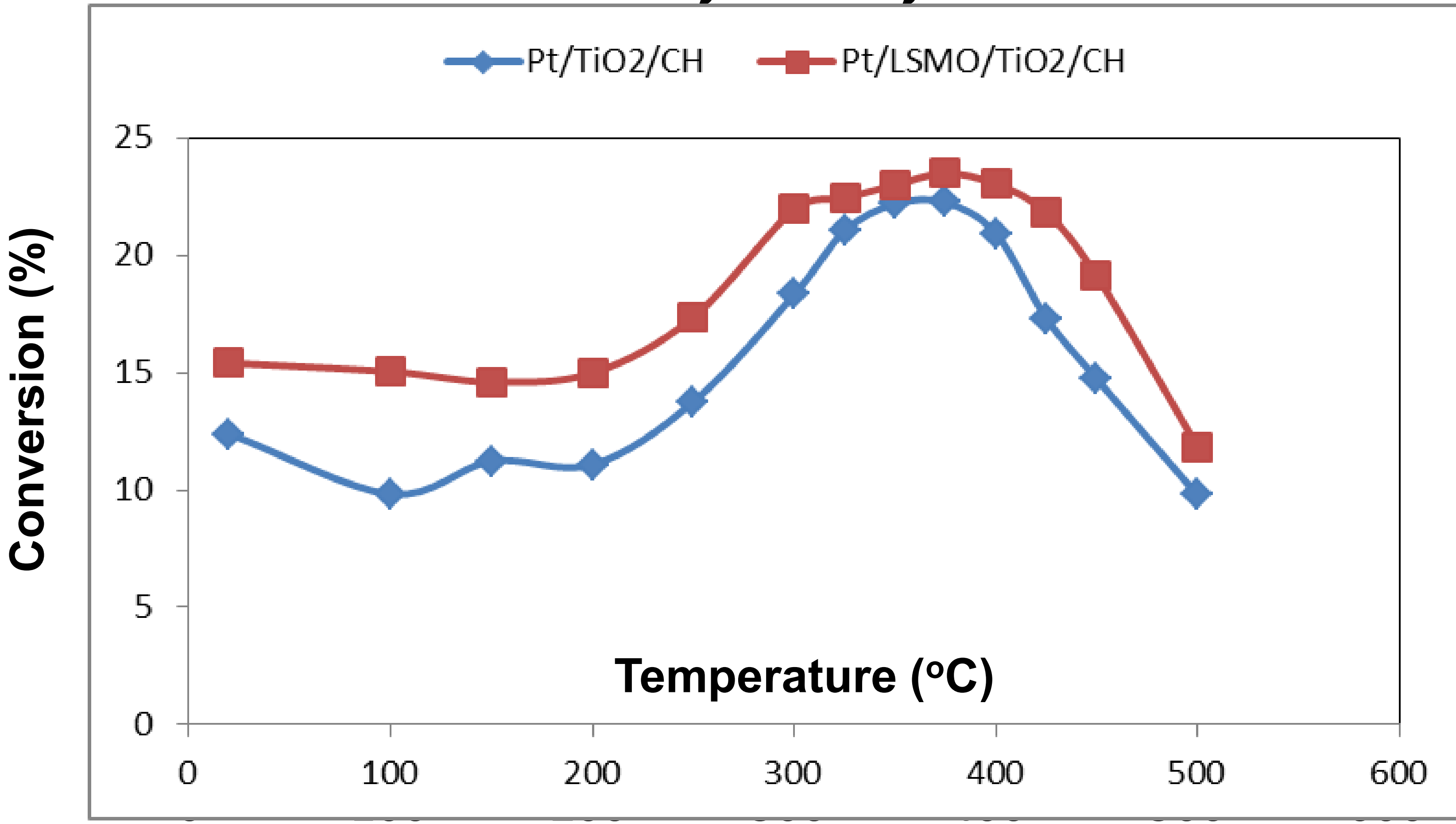
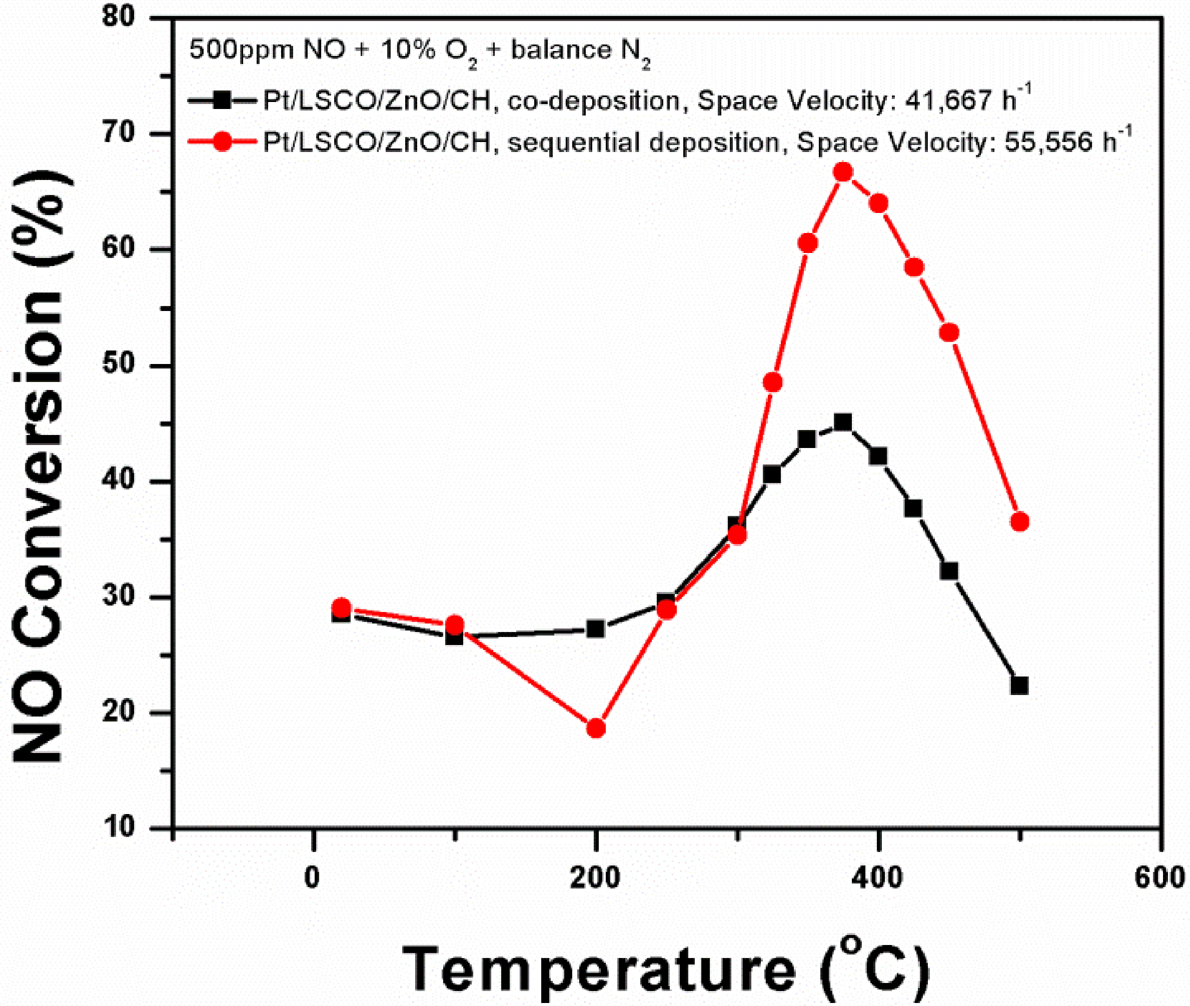


NO 500ppm, O_2 10%, N_2 balance; Pt: <1%; SV:166,667 h^{-1}

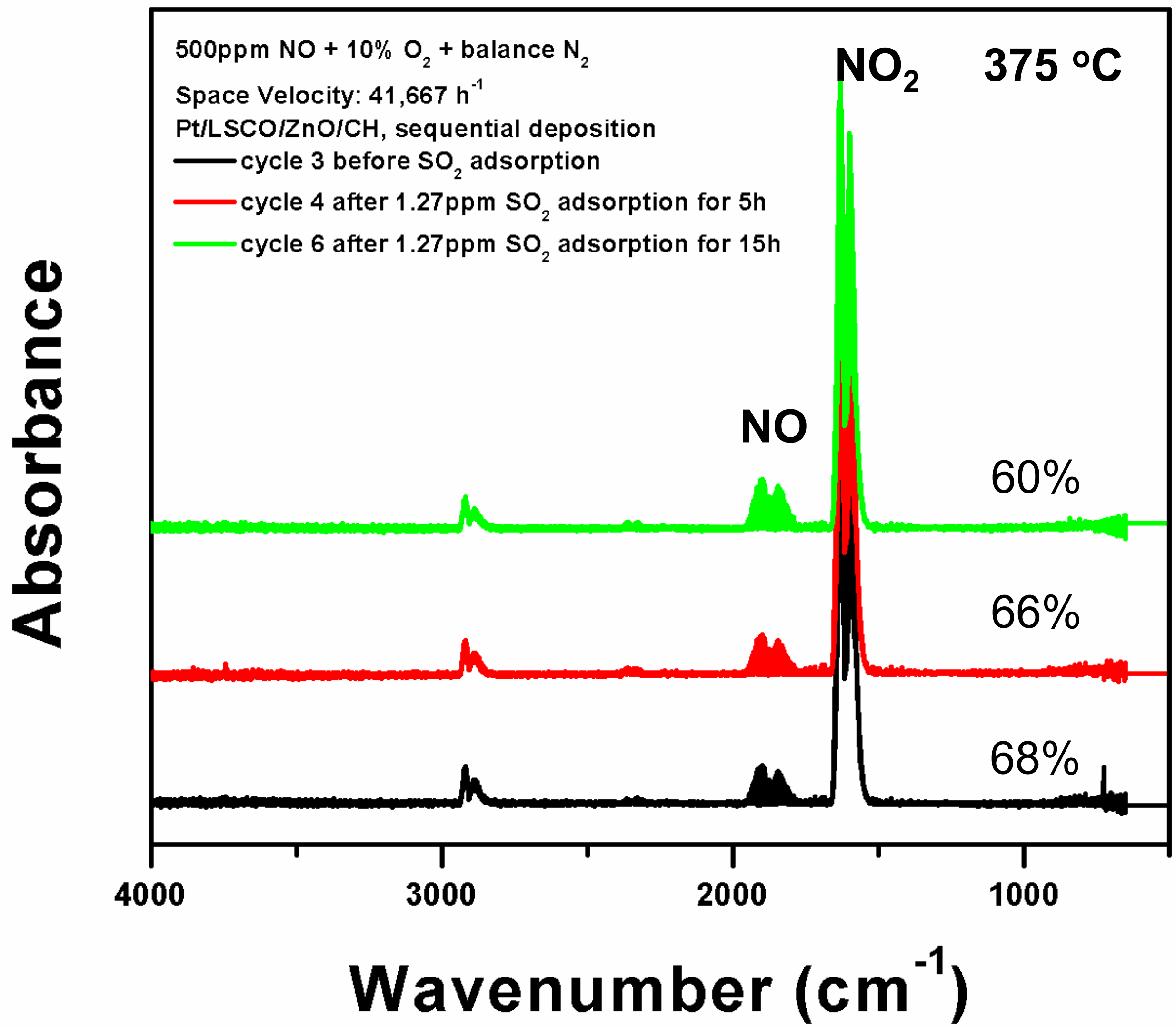
- ✓ LSCO loading in ZnO/Pt catalyst seems to reduce the NO oxidation performance;
- ✓ LSMO loading improved the NO oxidation;
- ✓ High space velocity induced low conversion efficiency

Composite nanowire array catalysts → NO oxidation



- ✓ Sequential deposition: 68%, medium space velocity;
- ✓ Co-deposition: 45%, medium space velocity;
- ✓ both peak at 375 °C.

Composite nanowire array catalysts → S-poisoning Resistance



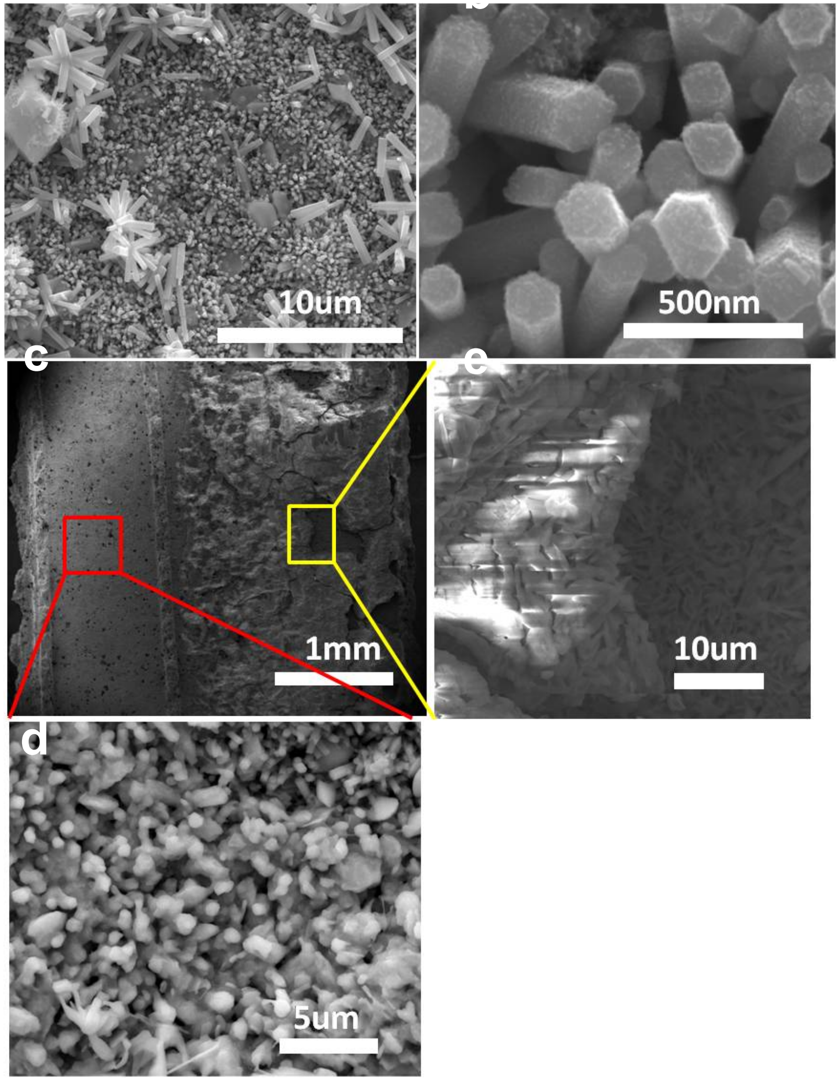
S-poisoning treatment: 1.27 ppm SO_2 at RT for 0-15 hours.

Composite nanowire array catalysts → NO_x storage and reduction

ZnO/LSCO/BaO/Pt, sequential loading, BaO ~10 wt.% over ZnO.

Inside channel

Outside surface



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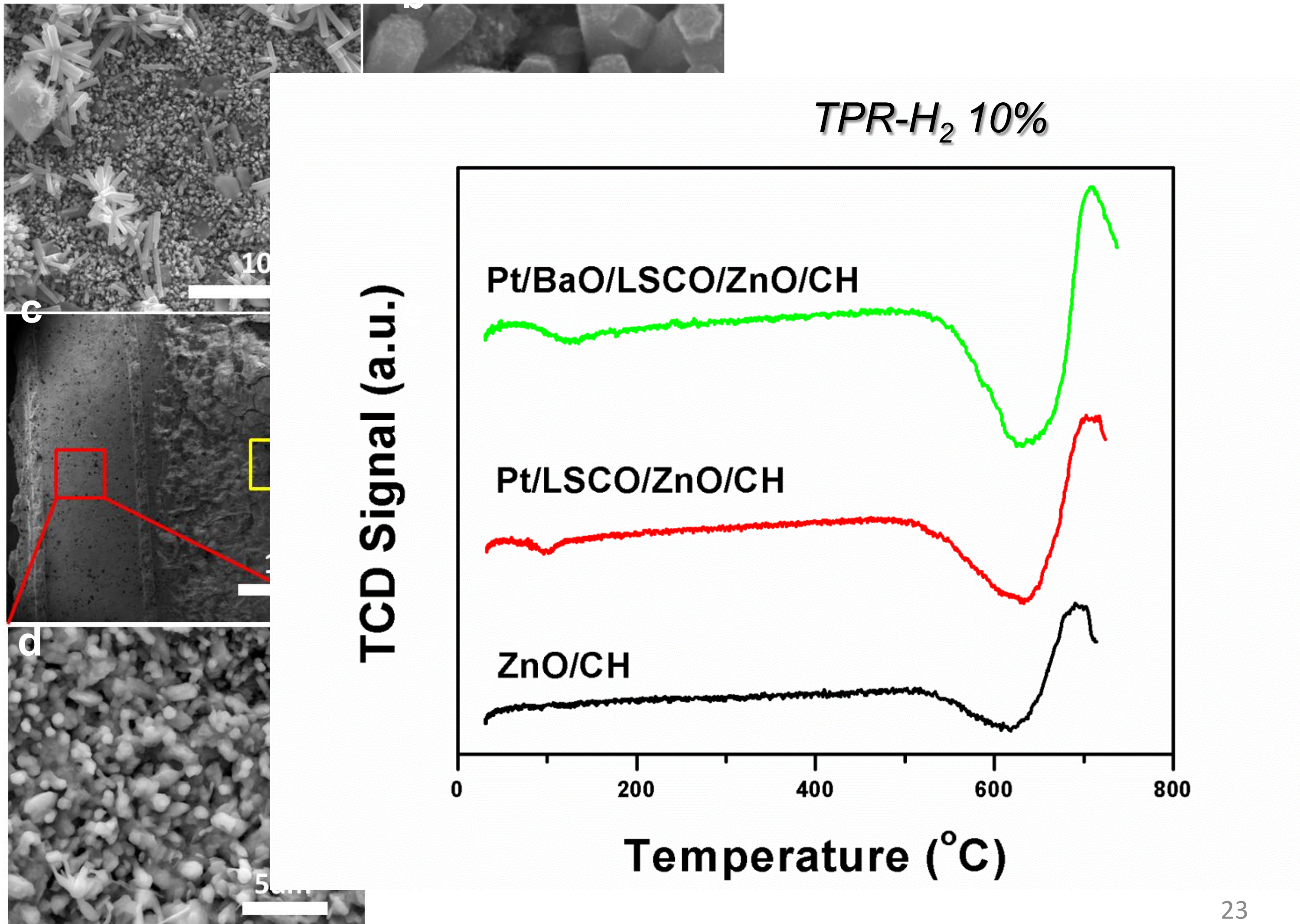

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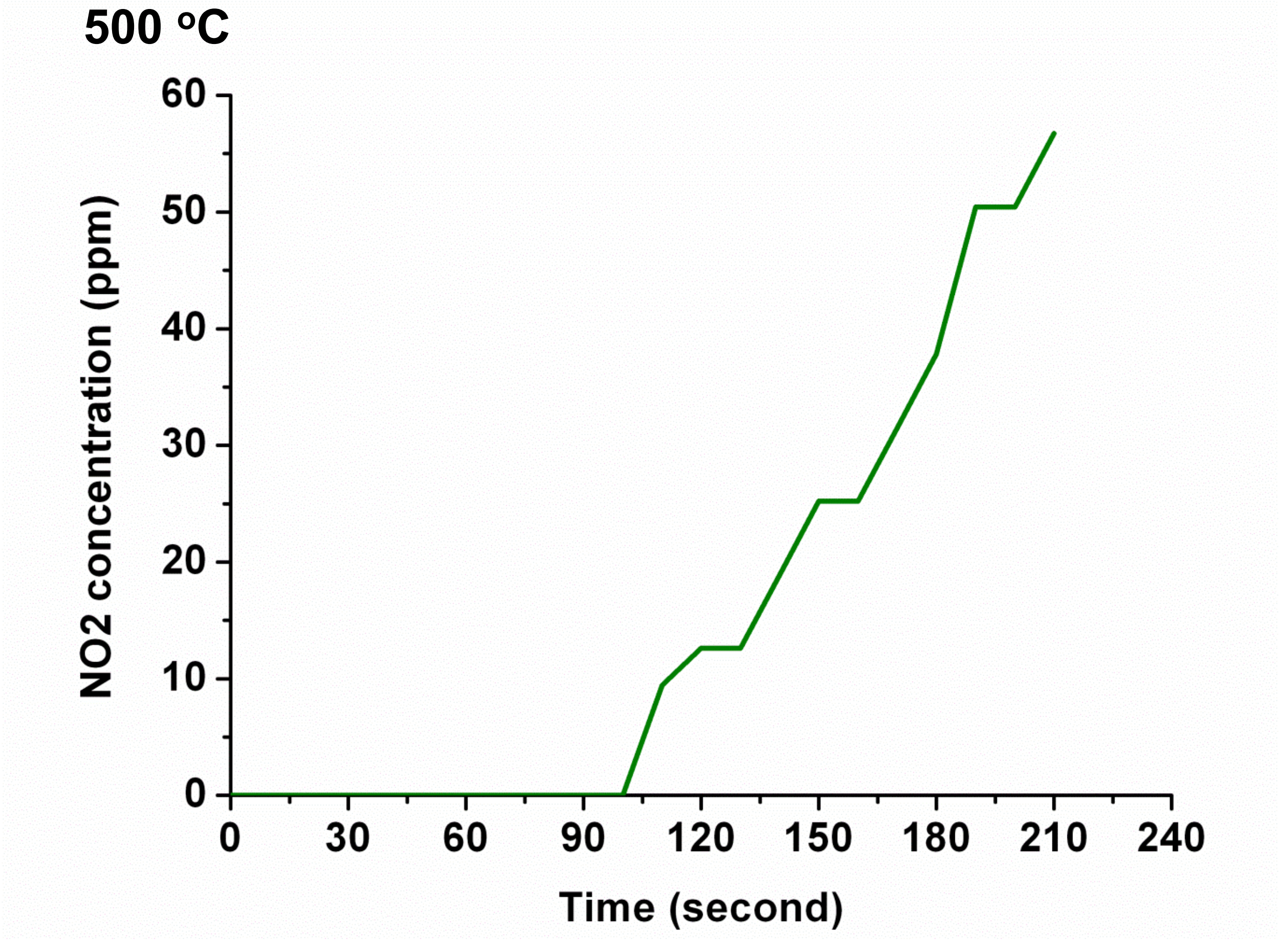

NO 500ppm, O_2 10%, N_2 balance (1300s) → NO 500ppm, H_2 5%, N_2 balance (800s)

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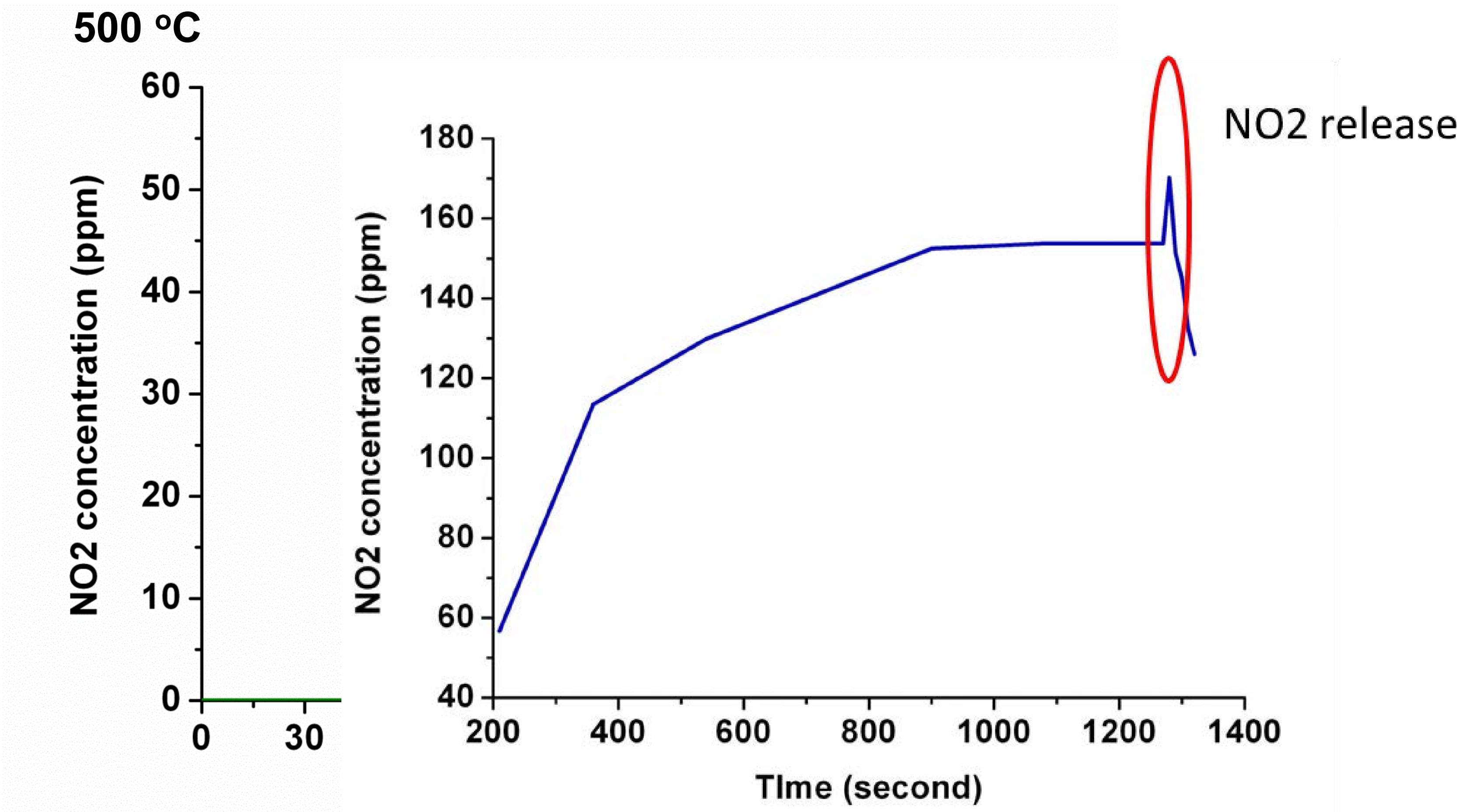

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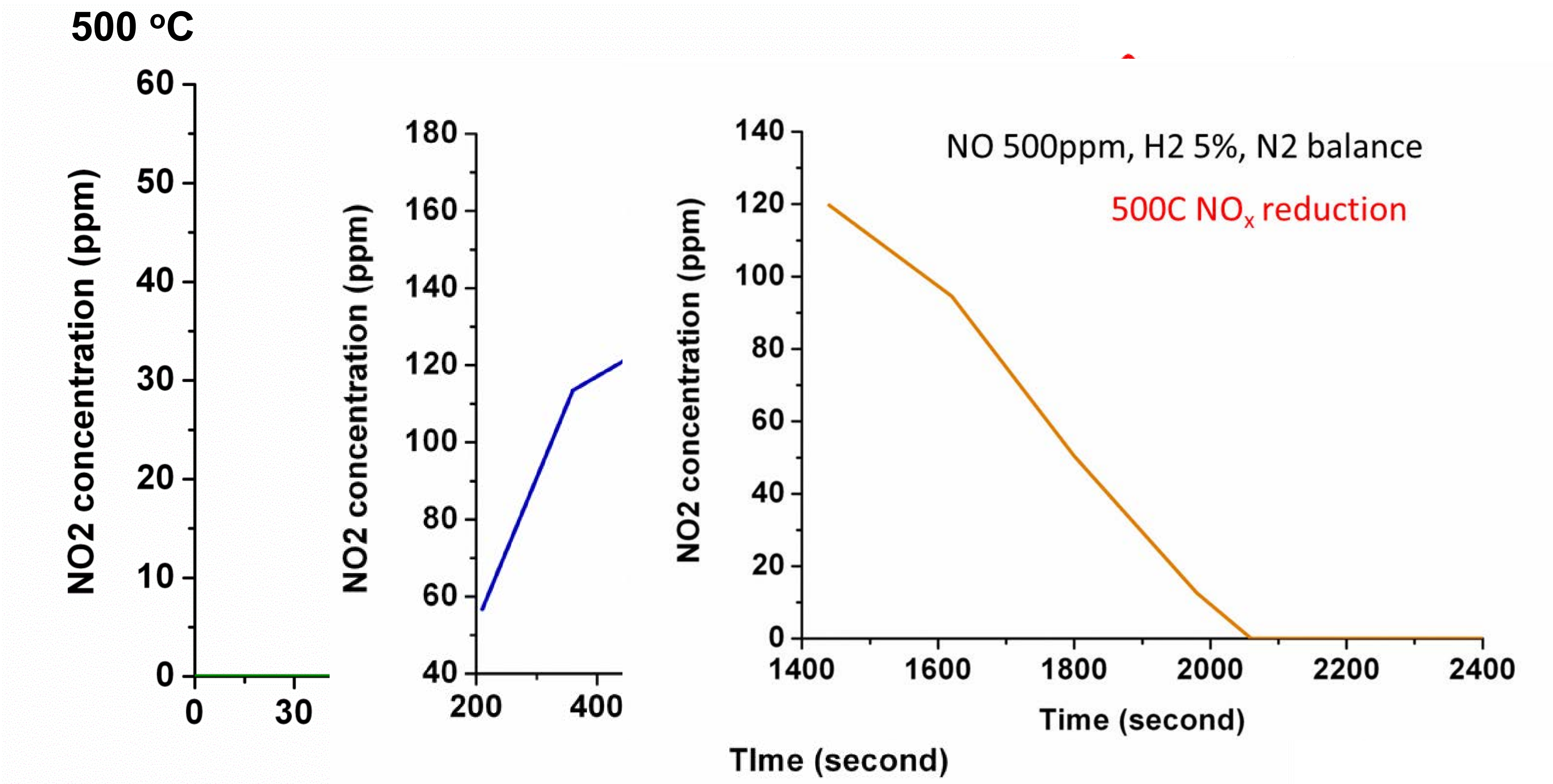

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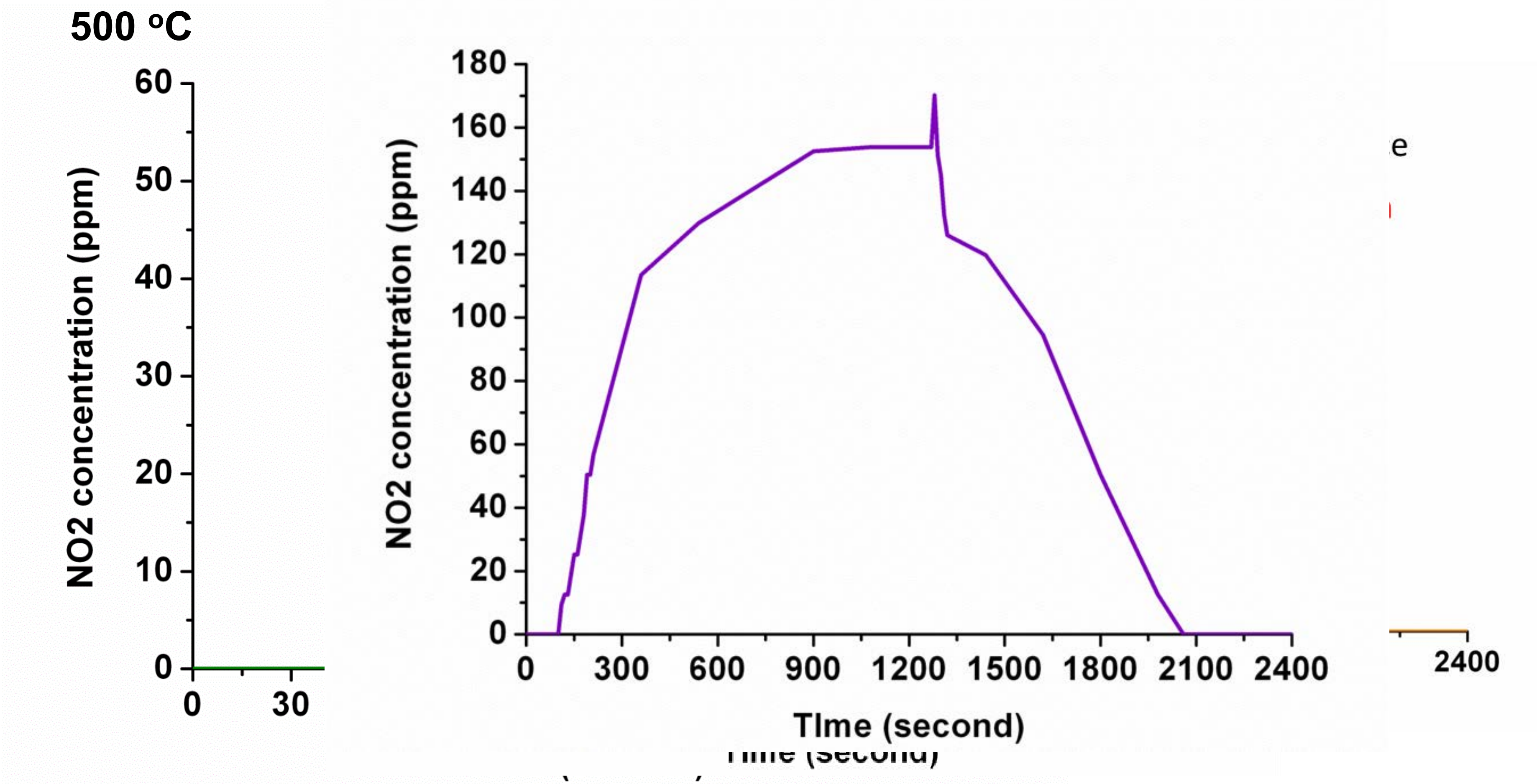


NO 500ppm, O_2 10%, N_2 balance (1300s) → NO 500ppm, H_2 5%, N_2 balance (800s)

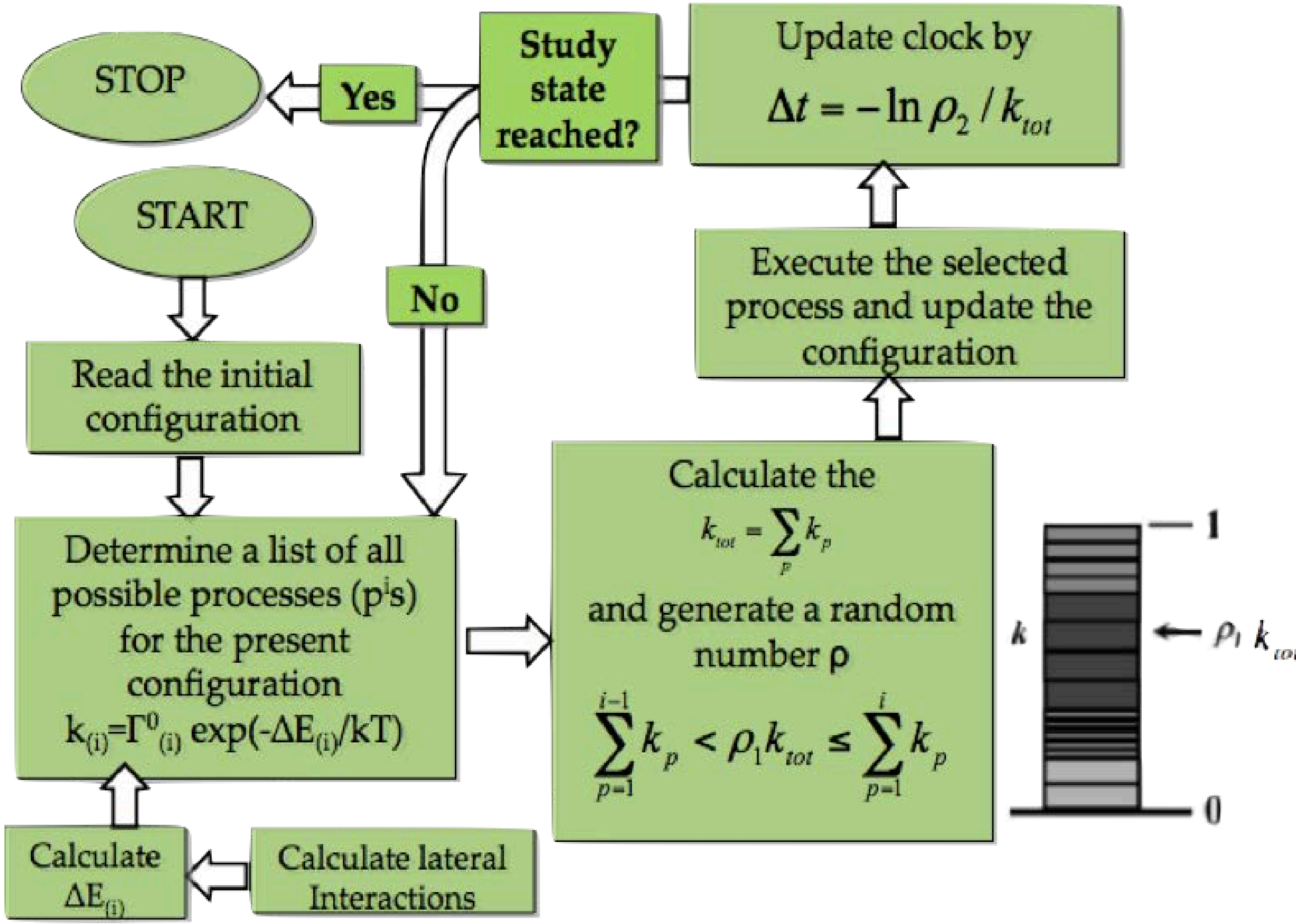
Kinetic Monte Carlo Simulations

Method Highlights

- DFT fitted 2-D lattice gas Hamiltonian
- Lateral interactions between the adsorbates
- Activation barriers within DFT nudged elastic band Method
- Local environment dependent activation barriers

Kinetic Monte Carlo Simulations

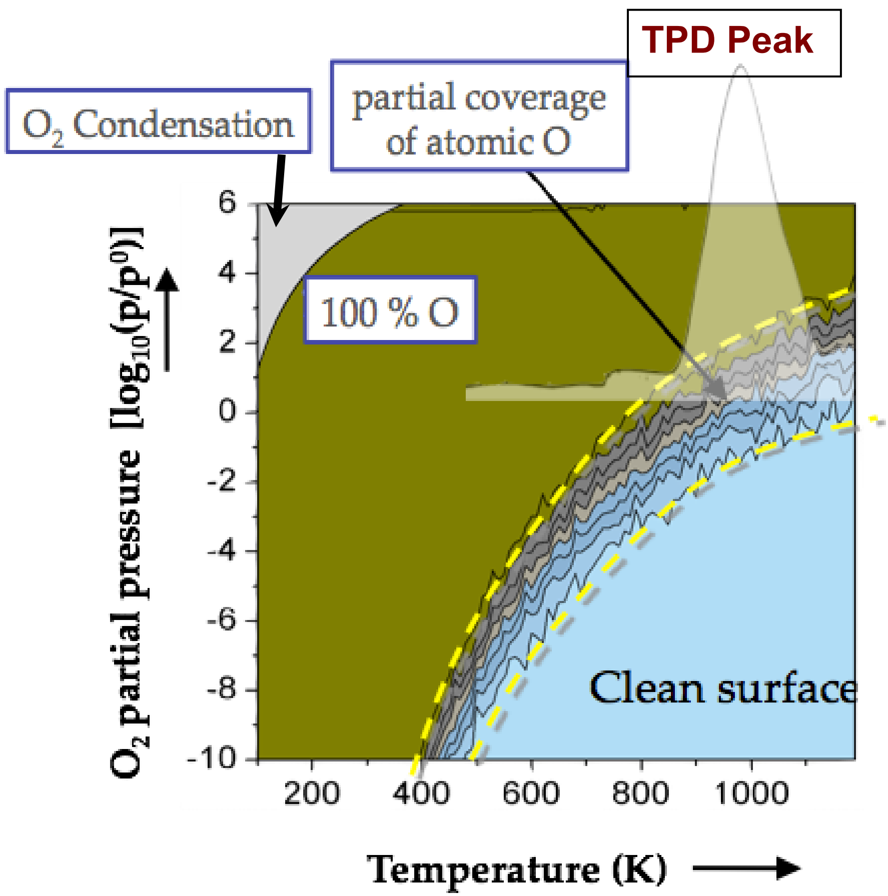
Algorithm



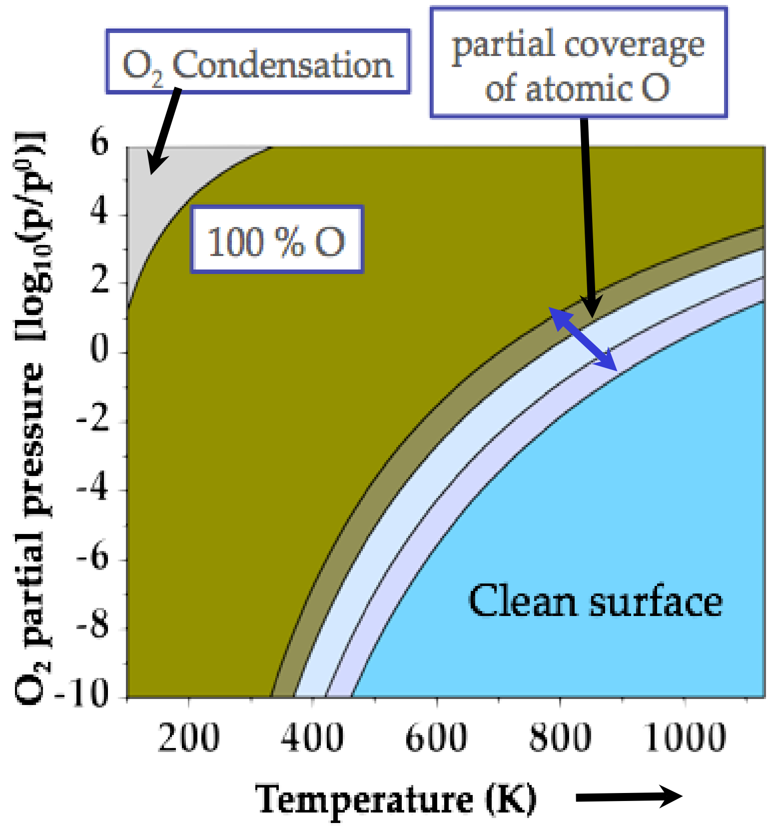
Kinetic Monte Carlo Simulations

Thermodynamic Phase diagram

a kMC generated



b FPT generated



TPD: Saracco, G., Geobaldo, F. (1999). Applied Catalysis B: Environmental.

Collaborations

- Honda Research Institute;
- United Technologies Research Center;
- Corning, Inc.;
- Umicore Autocatalyst USA;
- Brookhaven National Laboratory.

Future work

1) Continue the metal (oxide) loading/doping study on 3D composite nanowire arrays.
2) Evaluate the catalytic performance of 3D composite nanowire arrays on the hydrothermal stability, NO_x storage and reduction, S-poisoning resistance, and particulate matter filtering.
3) Further calculate the oxygen dynamics on the perovskite crystal surfaces associated with incorporation of NO_x interactions.

Acknowledgements

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